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MEASUREMENT OF FLUORIDE IN TOOTHPASTE

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INTRODUCTION

Samples of toothpaste have occasionally surfaced in the New York Laboratory for quantitation of fluoride content. Although it is not a tariff problem, there are FDA regulations on the amount of fluoride that toothpaste should contain. The FDA Compliance Department lists fluorinated toothpaste as containing 0.22%-0.24% sodium fluoride or 0.4% stannous fluoride, or 0.76% sodium monofluorophosphate, by weight. The sample used in the following experiment was labeled to contain sodium monofluorophosphate of unknown concentration. The possible problems in analyzing toothpaste include the solubility of the sample and the sample matrix. The quantitation of fluoride is also complicated by possible mixtures of stannous fluoride and sodium monofluorophosphate. The analytical methods available in the United States Pharmacopeia XXII (U.S.P.) and the "National Bureau of Standards Certificate of Analysis for Standard Reference Material 79a Fluorspar" were evaluated and adapted for the analysis of toothpaste.

The U.S.P. method for **Sodium Fluoride** is intended for assays of 98% to 102%. The assay procedure requires a fresh ferric chloride solution which is standardized by titrating with 0.1 N thiosulfate. The NaF sample is titrated with the $FeCl_3$ solution. This procedure is time consuming and is written to determine the fluoride concentration of 98% sodium fluoride. The amount of fluoride in toothpaste is significantly less than 98%.

The U.S.P. method for **Sodium Fluoride Oral Solution** has a criterion of "90-110% of the labeled amount of NaF." The assay procedure requires a buffer composed of (1,2-cyclohexylene dinitrilo)tetraacetic acid, glacial acetic acid, sodium chloride and sodium hydroxide. Standards of 190 ug/ml to 1.9 ug/ml are recommended. The potential in mV is measured with a fluoride ion specific electrode and a calomel reference electrode. A plot of the log of fluoride ion concentration vs. potential is used as a calibration curve to determine the sample concentration. Based

on the speculated fluoride concentration of 1mg/50ml, this procedure appears to be more appropriate for the determination of fluoride in toothpaste.

The method for determination of calcium fluoride in fluorspar, addressed in the National Bureau of Standards Certificate of Analysis, involves a lengthy sample preparation procedure because of the physical nature of fluorspar (natural calcium fluoride containing 85-98% calcium fluoride depending on the grade), but requires similar procedures, solutions and equipment for the calibration curve and data measurement.

EXPERIMENTAL

Equipment/Reagents

1. A commercial buffer manufactured by Corning (FAD - Fluoride Analysis Diluent) is used. Other commercially available buffers for fluoride ion analysis are also available. Corning FAD is used 1:1 as an ionic strength adjustor and buffer. It contains the ingredients listed in the U.S.P. procedure for Sodium Fluoride Oral Solution.

2. The standards are made from a commercially available standard - Corning Fluoride standard 100 ppm.

3. An Orion Model 96-09 fluoride ion specific combination electrode is used to measure the potential.

4. A stirring plate and a number of stirring bars and magnetic stirrers are necessary to homogenize the solution.

5. The Corning pH/eV meter 120 is used to measure the potential.

6. Distilled/deionized water (DW) should be used to minimize the effects of other ions and of fluoride already added to the water.

7. Plastic beakers and volumetric flasks, and glass pipets are used for dilutions and transfers.

Slope

Specific ion electrodes tend to have a limited life and should be tested after they have not been used for a while. The "slope" of the Orion electrode is determined as per the instructions in the Orion instruction manual.

Standard Calibration Curve

An aliquot of a 100ppm fluoride solution is quantitatively transferred to a plastic 100ml volumetric flask, and diluted to the mark with deionized water and buffer solution as follows:

Table I Fluoride Standards Potential Measurements

	100 ppm F^- (ml)	Deionized Water (ml)	Buffer (ml)	Potential (mV)
1.	1	49	50	84
2.	5	45	50	46
3.	10	40	50	28
4.	25	25	50	5

After the solutions are transferred to plastic beakers and homogenized with magnetic stirbars, the potentials are recorded. A calibration curve is plotted from the potentials vs. the log of the fluoride concentration.

Sample Preparation

This study involved a single toothpaste sample prepared in triplicate. Each of the replicates was prepared as follows. Approximately one gram of sample toothpaste is weighed into a plastic beaker. 50ml FAD buffer is added. The sample is stirred using magnetic stirring bars until the solution is apparently homogenized. The solution is quantitatively transferred to a plastic 100ml volumetric flask and diluted to the mark with deionized water. The solution is returned to the plastic beaker and the potential is recorded after the reading has stabilized.

Normally, to compensate for the effect of sample matrix on analyte response, a standard and a blank with a similar matrix are used. But in this case, a known toothpaste without fluoride is unavailable, and the toothpaste matrix is comprised of various substances in unknown amounts. Instead, in order to test for the effect of the matrix, a sample was spiked with a known fluoride amount, and the observed increase in fluoride concentration was compared with that calculated.

RESULTS AND DISCUSSION

A spreadsheet program (EXCEL) is used to graph the standard data and to calculate a best fit line using linear regression. The potential is plotted against the log of the fluoride ion concentration.

GRAPH:

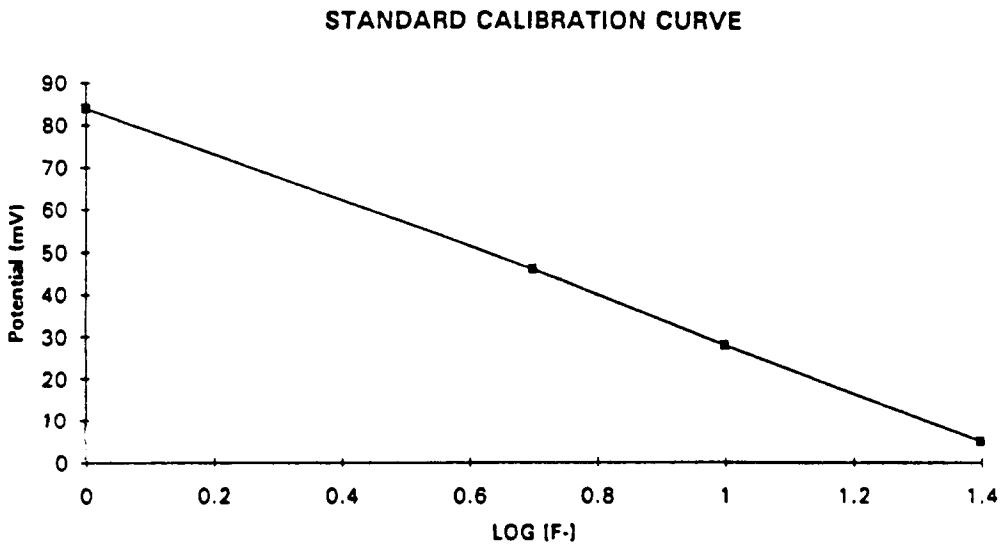

Table II Fluoride Standards Calculated Concentrations

Standards		Potential	Calculated
[F^-] (ppm)	LOG[F^-]	(mV)	[F^-] (ppm)
25	1.39794	5	25.51925
10	1	28	9.99665
5	0.69897	46	4.8009
1	0	84	1.02062

Regression results:

The equation of the best line fit represented by the slope-intercept formula (y = mx + b) is:

$$y = -56.50919x + 84.50097$$

R-squared, a measure of the linearity of the data, is 0.99955, 1 being a perfect fit.

By substituting the potential (y), the log of the fluoride ion concentration (x) can be found. The antilog will yield the concentration of fluoride ion in the sample solution as ppm.

The percent fluoride in the toothpaste by weight can be determined by the following equation:

$$\%F = [C(ppm) * V_f(ml) * 10^{-6} / \text{Sample Wt. (g)}] * 100$$

C(ppm) = F^- concentration in ppm (determined by experiment)
V_f(ml) = final volume of analytical solution in ml (100ml)
10^{-6} = factor to convert from micrograms to grams
100 = converts fraction to percentage

Table III Sample Calculations and Results

Sample	Sample Weight (g)	Potential (mV)	Calculated [F-] (ppm)	%F- in sample	%MFP in sample
1	1.1681	46	4.80089	.04109	.31129
2	1.0209	48	4.42517	.0433	.32803
3a	1.0186	49	4.24848	.04171	.31598
				Standard Deviation	0.008635
3b	3a + 1ml	44	5.20852		

To determine whether the matrix affects the calibration curve, a spiked sample (3b) is compared to the original sample (3a). The spiked sample is the original sample with 1 ml of 100 ppm F^- solution added. The expected increase in concentration from the spike is 0.9901 ppm based on a volume of 101 ml from the addition of 1 ml 100 ppm F^- to 100 ml sample solution. Applying a volume of 101 ml to the original sample concentration of 4.24848 ppm yields a concentration of 4.20642 ppm. The total concentration of the spiked sample, calculated from the linear regression, is 5.20852 ppm. The difference between the spiked and unspiked calculated results is 1.00210 ppm compared to theoretical 0.99009 ppm. The two values have a difference of 0.01201 ppm, or approximately 1.2%. The small error can be considered negligible and may be due to experimental error.

If the fluoride is present in toothpaste in the form of sodium monofluorophosphate (MFP, Na_2PO_3F), then to compare the experimental concentration of fluoride to the concentration of MFP labeled on the tube or box, the fraction of fluoride in MFP must be calculated. The molecular weight of MFP is 144 and the atomic weight of fluoride is 19.

$$\text{Fraction of fluoride in MFP: } \frac{\text{AW } F^-}{\text{MW MFP}} = \frac{19}{144} = .132$$

The final part in the analysis is to divide the concentration of fluoride in the sample by the fraction of fluoride in MFP to yield the concentration of MFP in the sample.

$$\%\text{MFP} = \%\ F^-/0.132$$

Fluoride is present in toothpaste normally as sodium monofluorophosphate. The sample was also ashed and analyzed by emission spectrometry for cations. No trace of tin from stannous fluoride was found.

CONCLUSIONS

The calibration curve of potential vs. log of fluoride concentration has been shown to be valid using linear regression. The sample matrix does not appear to affect the measurement of fluoride ion as indicated by the spiked samples. This procedure was developed as an exercise in adapting published methods for different applications.

REFERENCES

1. The United States Pharmacopeia, 22nd Ed., The United States Pharmacopeial Convention, Inc., Rockville, Maryland, 1989. pp. 1259-1260.

2. Orion Model 94-09, 96-09 Fluoride/Combination Fluoride Electrodes Instruction Manual, Orion Research Incorporated, Boston, Massachusetts, 1991, pp.5,6,10-12.

3. "National Bureau of Standards Certificate of Analysis Standard for Reference Material 79a Fluorspar"